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Microstructural control of porous Al_2TiO_5 by using potato starch as pore-forming agent

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In this study, we have tried to prepare porous Al_2TiO_5 ceramics with potato starch as a pore-forming agent at relatively low sintering temperatures by reactive sintering method using fine-grained starting materials. α-Al_2O_3 powder (0.1 μm) and TiO_2 rutile powder (2 μm) were wet-ball milled in ethanol for 2 h in a planetary ball-mill. The mixed powder was blended with 5–30 wt % of potato starch powder in an agate mortar with ethanol. Green samples with no binder were sintered at 1300–1500°C for 2 h in air. The sample contained finer closed pores (<1 μm) as well as the larger pores (5–80 μm). The finer microstructure formation can be explained by (1) the local heating effect via the combustion of potato starch, and (2) water vapor-assisted effect.

Key-words : A: Sintering, B: Porosity, D: Al_2TiO_5, E: Thermal application

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1. Introduction

Al_2TiO_5 has an orthorhombic pseudobrookite-type structure with a chemical formula of A_2BO_5.[1] Microcracks occur frequently in polycrystalline Al_2TiO_5 due to the uniaxial anisotropy of thermal expansion. These microcracks contribute to its prominent low thermal expansion and result in its good thermal shock resistance.[2),3] On the other hand, the microcracks also deteriorate mechanical properties.[4),5] Although Al_2TiO_5 has a high melting point of 1860°C, it decomposes to α-Al_2O_3 and rutile-type TiO_2 at 750–1300°C.[2)–5] Al_2TiO_5 is used as a coating material, an oxidation resistant material and an insulating material under high temperatures, because of its low thermal expansion, thermal shock resistance and corrosion resistance. Recently, porous Al_2TiO_5 is also applied for third-generation diesel particulate filters (DPF).[6)–8] Corning (USA)[6] and Sumitomo Chemical (Japan)[7] have developed the DPF using Al_2TiO_5 with some dopants.

In order to control the pore-size distribution of porous materials, pore-forming agents are often added to starting powders. Starches are selected as the pore-forming agent with low environmental impact.[9)–11] They burnt out at lower temperatures than sintering temperatures of various ceramics. The burn-out process only emits CO_2 and H_2O, resulting less damage not only to furnaces but also to outer environment. In addition, starches are available at low cost.

In 2012, Hongzhi et al. reported the synthesis of porous Al_2TiO_5 ceramics by reactive sintering.[12] In their report, reactive sintering at 1400–1500°C using Al_2O_3 (10–30 μm) and TiO_2 (2–10 μm) powders as raw materials and corn starch (5–20 μm) as pore-forming agent was used to prepare the porous Al_2TiO_5. They reported that the sintered products had a bimodal-pore structure with the diameter of 50–200 μm and 2–6 μm, however, the detail of pore-structure characterization was not given in detail.[12]

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In order to apply the reactively-sintered porous Al_2TiO_5 ceramics for light-weight structural materials or DPF materials, it is needed to obtain finer and more homogeneous porous structure with higher mechanical properties. In this study, we have tried to prepare porous Al_2TiO_5 ceramics with potato starch as a pore-forming agent at relatively low sintering temperatures by the reactive sintering method using fine-grained starting materials. It is worthy of note that no additives such as Fe_2O_3 or SiO_2 was added as dopant to obtain purer Al_2TiO_5 phase.

2. Experimental

2.1 Optimization of porous Al_2TiO_5 sintering temperature

As the starting material, α-Al_2O_3 powder (0.1 μm, 99.99% purity, TM-D, Taimei Chemical Co. Ltd., Saitama, Japan), and TiO_2 rutile powder (2 μm, 99.9% purity, Kojundo Chemical Laboratory Co. Ltd.) were used in expectation of less volumetric shrinkage. An Al_2O_3 powder and a TiO_2 powder (Al:Ti = 2:1 in mole fraction) were wet-ball milled in ethanol for 2 h in a planetary ball-mill (acceleration: 4*g*). The mixed slurry was dried, and then dry-ball milled for 2 h in polyethylene bottle. The obtained mixed powders were sieved through a 100-mesh screen (<150 μm). To obtain bulk porous Al_2TiO_5, the mixed powder was mold-pressed at 11.3 MPa. Then, green pellets of ~1 g with no binder, ~15 mm in diameter and ~3 mm in thickness, were sintered at 1200–1600°C for 2 h in air. **Figure 1** shows a schematic illustration of experimental procedure. The constituent phases of the bulk materials were analyzed by X-ray diffractometry (XRD, Multiflex, Cu-Kα, 40 kV and 40 mA, Rigaku, Japan).

2.2 The effect of potato starch addition as a pore forming agent

The mixed powder of α-Al_2O_3 and TiO_2 rutile in section 2.1 was blended with 5–30 wt % of potato starch powder (Wako Pure Chemical Industries Ltd.) in an agate mortar with ethanol. **Figures 2**(a) and 2(b) show a SEM image and TG–DTA curves of potato starch, respectively. The TG–DTA results clearly

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showed that the decomposition of potato starch completed at ~500°C. The mixed powder was dried, and sieved through a 100-mesh screen. The green body was obtained by mold-pressing at 11.3 MPa. Then, green pellets (~1 g with no binder, ~15 mm in diameter and ~3 mm in thickness) were sintered at 1300–1500°C for 2 h in air.

Bulk density of sintered pellets was measured from dimension and mass. The microstructure of porous Al_2TiO_5 was characterized using scanning electron microscopy (SEM, TM3000 Tablemicroscope, Hitachi, Japan). Bulk thermal expansion was evaluated by thermomechanical analysis (TMA, Thermo plus EVO II, Rigaku, Japan). Fracture strength was measured by three-point bending test (AG-I 20 kNT, Shimadzu, Japan), with span of 30 mm and crosshead speed of 0.5 mm/min. Samples with the dimension of 3 × 4 × 40 mm (JIS R1601) were used for the bending test.

3. Results and discussion

3.1 Optimization of porous Al_2TiO_5 sintering temperature

The XRD patterns of the samples sintered without starch are shown in **Fig. 3**. At 1200°C, only α-Al_2O_3 and TiO_2 rutile, same as the starting materials, were observed. At 1300°C, Al_2TiO_5 formation was confirmed and its peak intensities increased with increasing sintering temperature. The single phase Al_2TiO_5 was obtained at 1600°C. However, the sample sintered at 1600°C was easily broken into granules. So, although some Al_2O_3 and TiO_2 remained, sintering temperatures of 1300–1500°C were used for following experiments.

XRD patterns of Al_2TiO_5 samples with potato starch sintered at 1300°C are shown in **Fig. 4**. With 10 wt % starch addition, the formation of Al_2TiO_5 phase was slightly inhibited probably due to the less contact of Al_2O_3 and TiO_2 particles. Whereas, with 20 wt % addition, the formation of Al_2TiO_5 phase was accelerated, which might be explained that (1) the local heating effect by the combustion of potato starch, and (2) water vapor-assisted effect.[13)–15)] Since we have used a box-type furnace, a part of the water vapor, yielded from the combustion of potato starch, may remain in the sintering atmosphere.

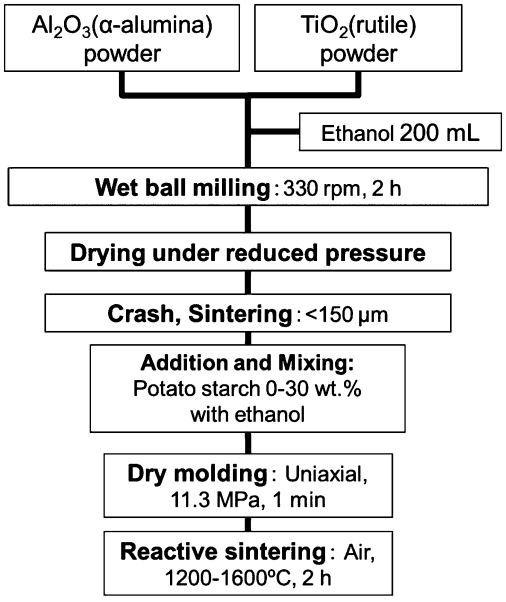

Fig. 1. Sample preparation process of porous Al_2TiO_5.

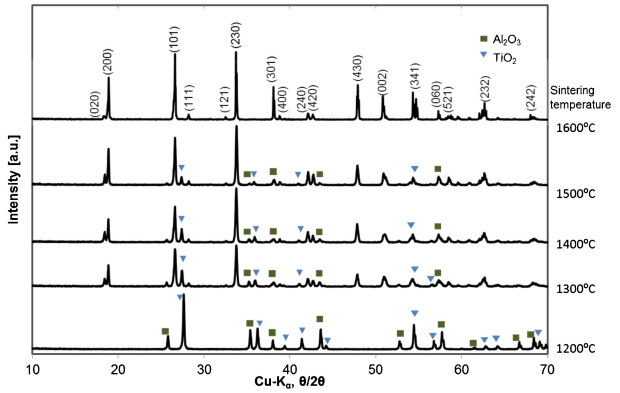

Fig. 3. XRD patterns of Al_2TiO_5 samples without starches at different temperatures.

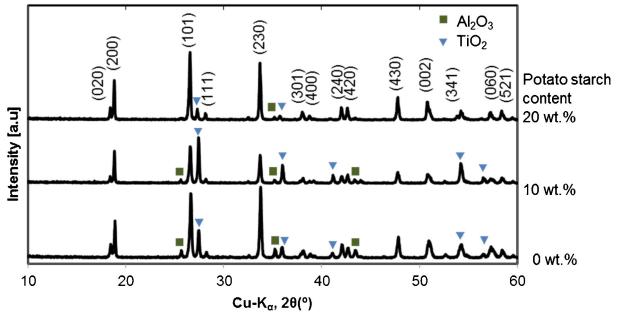

Fig. 4. XRD patterns of Al_2TiO_5 samples with potato starch sintered at 1300°C.

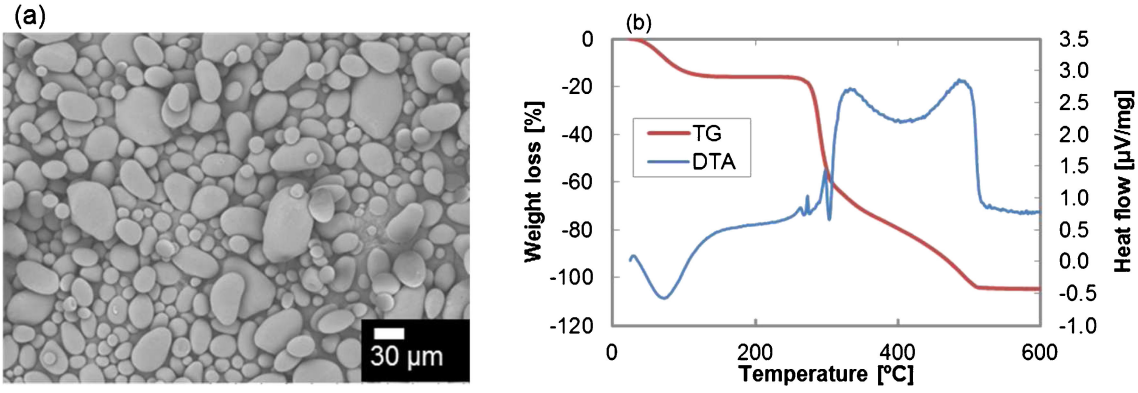

Fig. 2. (a) SEM image and (b) TG–DTA curves of potato starch.

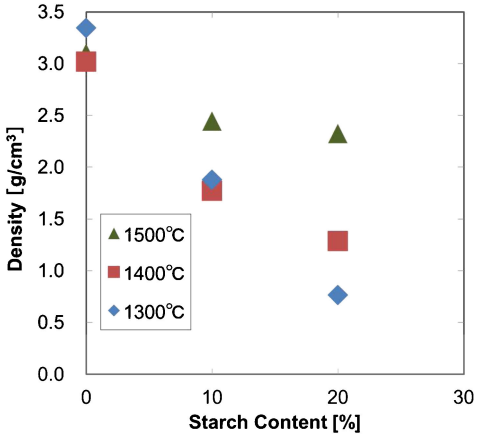

Fig. 5. Bulk density of porous Al_2TiO_5 sintered with different amount of potato starch.

3.2 The effect of potato starch addition as the pore forming agent

Figure 5 shows the bulk density of pellets sintered with different amount of potato starch. With increasing amount of potato starch, the bulk density was decreased. As for the pellets without starch, the pellet sintered at 1300°C had the highest bulk density. On the contrary, as for the pellets with 20 wt % potato starch, the pellet sintered at 1300°C had the lowest density. The difference between the samples with or without potato starch at 1300°C can be attributed to the residual Al_2O_3 and TiO_2 for non-starch sample; Al_2TiO_5 phase ($d = 3.69\,g/cm^3$) was less dense than initial Al_2O_3 ($d = 3.99\,g/cm^3$)/TiO_2 ($d = 4.25\,g/cm^3$) phases. It is noteworthy that the pellets sintered with ≥25 wt % potato starch were pulverized easily.

Microstructure of Al_2TiO_5 pellets sintered with/without potato starch is shown in **Fig. 6**. As for samples sintered at 1300°C, the pellet sintered without potato starch had fine and homogeneous microstructure with some microcracks [Fig. 6(a)]. At a high magnification, it is revealed that the pellet contained finer pores with the size of ~1 µm. The pellets sintered with potato starch [Figs. 6(b) and 6(c)] had larger pores with the size of ca. 5–80 µm, and the larger pores increased with increasing potato starch content. Equi-axed finer grains were often found in Fig. 6(b) at a higher resolution. These grains can be attributed to un-reacted TiO_2 and Al_2O_3 grains, which is in good agreement with the XRD analysis (Fig. 4). In Fig. 6(c), the sample contained finer closed pores (<1 µm) as well as the larger pores similar to Fig. 6(b). The finer microstructure formation can be also explained by (1) the local heating effect via the combustion of potato starch, and (2) water vapor-assisted effect, as explained for Fig. 4.

As for samples sintered at 1500°C, the pellet sintered without potato starch contained about 3 µm sized closed pores [Fig. 6(d)]. The size increment of pores in comparison with Fig. 6(a) can be simply explained by the coalescence of pores with increasing sintering temperature. With 10 wt % potato starch addition [Fig. 6(e)], the microstructure was similar to that of 1300°C. XRD result for the 10%-sample sintered at 1500°C (not shown) indicated that un-reacted TiO_2 and Al_2O_3 still remained like as the 10%-sample sintered at 1300°C [Fig. 6(b)]. The pellet with 20 wt % potato starch had pores with apparent size of ~1–15 µm [Fig. 6(f)]. Al_2TiO_5 grains became larger with increasing the sintering temperature. The empty space formed by the combustion of potato starch may offer Al_2TiO_5 grains to be enlarged.

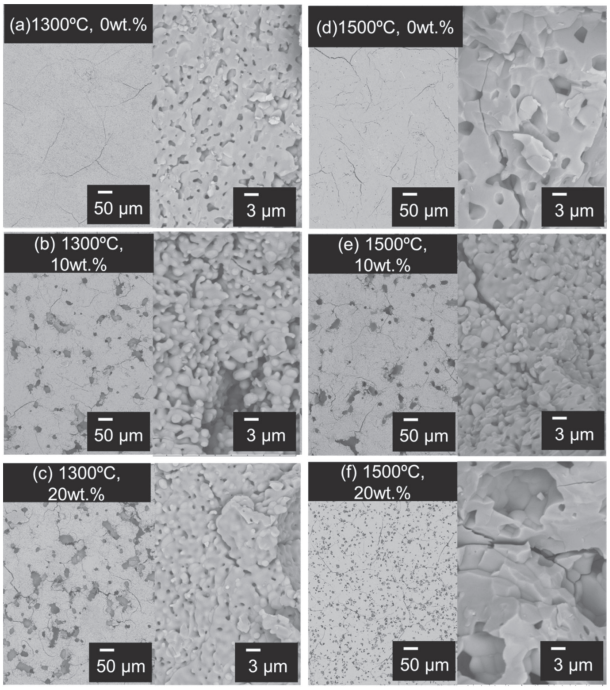

Fig. 6. Microstructure of Al_2TiO_5 pellets sintered with potato starch: (a)1300°C, 0 wt %, (b) 1300°C, 10 wt %, (c) 1300°C, 20 wt %, (d) 1500°C, 0 wt %, (e) 1500°C, 10 wt % and (f) 1500°C, 20 wt %.

Table 1. Three-point bending strength of porous Al_2TiO_5 with potato starch

Starch Content [%]	Bending Strength [MPa]		
	1300°C	1400°C	1500°C
0	50	10	8
10	19	8	6

With increasing the amount of potato starch addition, microcracks seem to connect the large pores.

Table 1 summarizes the 3-point bending strength of porous Al_2TiO_5 with potato starch. Since the samples sintered with ≥20 wt % of potato starch easily broke into small pieces, their bending strength were not measured. As for the samples without potato starch, bending strength sintered at 1300°C was 50 MPa. With increasing sintering temperature, bending strength decreased as 10 and 8 MPa for 1400 and 1500°C, respectively. With 10 wt % potato starch, bending strength were 19, 8, and 6 MPa for 1300, 1400 and 1500°C, respectively. The decrease of bending strength with increasing sintering temperature is attributable to the microcrack formation coincident with the Al_2TiO_5 formation. According the report by Hongzhi et al.,[12] the Al_2TiO_5 sample containing SiO_2 and Fe_2O_3 additives sintered at 1500°C with 10 wt % potato starch had the bending strength of 9.5 MPa. Further effort will be needed to improve the mechanical properties of un-doped porous Al_2TiO_5.

Figure 7 and **Table 2** show the difference of thermal expansion between with/without potato starch addition. It is clear that the sample with potato starch exhibited almost identical thermal expansion behavior as that without starch.

4. Conclusions

In this study, we have successfully prepared un-doped porous Al_2TiO_5 ceramics with potato starch as a pore-forming agent at

Table 2. Thermal expansion of Al_2TiO_5 with/without potato starch

Starch content [0 wt %]			Starch content [10 wt %]		
Temperature [°C]	Expansion (ΔL/L)[%]	CTE × 10^7 [1/K]	Temperature [°C]	Expansion (ΔL/L)[%]	CTE × 10^7 [1/K]
50	0.003	8.63	50	−0.001	−2.37
100	−0.002	−2.46	100	−0.007	−9.02
150	−0.009	−6.61	150	−0.014	−10.58
200	−0.015	−8.06	200	−0.018	−10.31
250	−0.022	−9.61	250	−0.028	−12.35
300	−0.029	−10.41	300	−0.032	−11.63
350	−0.035	−10.61	350	−0.036	−11.05
400	−0.039	−10.34	400	−0.040	−10.48
450	−0.041	−9.56	450	−0.041	−9.52
500	−0.041	−8.48	500	−0.040	−8.43
550	−0.041	−7.67	550	−0.040	−7.60
600	−0.039	−6.78	600	−0.038	−6.63
650	−0.036	−5.76	650	−0.035	−5.50
700	−0.031	−4.62	700	−0.029	−4.29
750	−0.025	−3.42	750	−0.022	−3.07
800	−0.017	−2.20	800	−0.014	−1.86
850	−0.013	−1.55	850	−0.009	−1.12
900	−0.007	−0.82	900	−0.003	−0.39
950	0.006	0.62	950	0.010	1.05

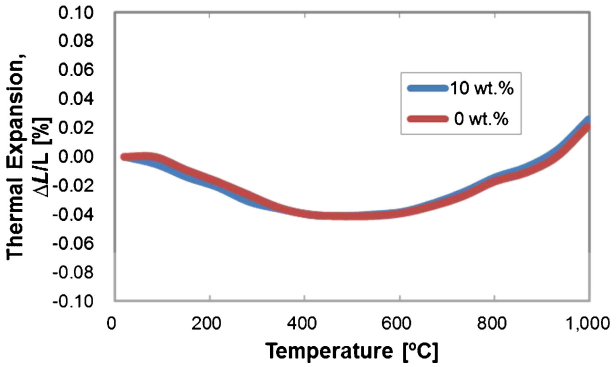

Fig. 7. Thermal expansion of Al_2TiO_5 at different amount of potato starch.

relatively low sintering temperatures (1300–1500°C), by reactive sintering method using fine-grained starting materials. The pellets sintered at 1300°C with potato starch had larger pores with the size of ca. 5–80 µm, and the larger pores increased with increasing potato starch content. The sample with 20 wt % potato starch contained finer closed pores (<1 µm) as well as the larger pores. The finer microstructure formation can be explained by (1) the local heating effect via the combustion of potato starch, and (2) water vapor-assisted effect. It is revealed that the sample with potato starch exhibited almost identical thermal expansion behavior as that without starch.

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